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Barium flux in the Southern Ocean (Atlantic sector)

INTRODUCTION

Chemical analyses were carried out within particulate matter from sediment traps, which will further assess the reliability of the barium/barite signal as an indicator for productivity. During the last fifteen years, the search for geochemical tracers which allow the reconstruction of the chemical characteristics of the oceans, past climates, and paleoproductivity was intensified (e.g., ELDERFIELD, 1991). These attempts revealed that marine sediments from upwelling areas show enhanced barite concentrations (e.g., VON BREYMANN *et al.*, 1992). The apparent covariance between the barite concentration and an enhanced surface productivity (e.g., DEHAIRS *et al.*, 1980; BISHOP, 1988) suggests that barium may be applied as an indicator for siliceous plankton productivity (e.g., DYMOND *et al.*, 1992).
The similarity of the dissolved barium profile to silica and alkalinity profiles points to the involvement of barium into the biogenic cycle (CHAN *et al.*, 1977). Apparently, barium is removed from surface waters and precipitates as barite within sinking biogenic particles, which subsequently dissolve in the deeper water column and in the sediment. Nevertheless, the process by which barite forms within the water column is still not known. According to several authors (CHOW and GOLDBERG, 1960; DEHAIRS *et al.*, 1980; BISHOP, 1988), barite formation takes place within microenvironments within the water column, where the organic matter of planktic cells or fecal pellets and aggregates decompose. Either the excess sulfate results from the decay of labile sulfur in the organic matter (CHOW and GOLDBERG, 1960; DEHAIRS *et al.*, 1980; BISHOP, 1988) or the excess barium release results from the dissolution of celestite. Celestite ($SrSO_4$) is provided by the marine planktonic protozoan group Acantharia (BERNSTEIN *et al.*, 1992).

MATERIAL AND METHODS

The flux data originate from one-year time series sediment traps from Bransfield Strait (KG1, KG2, and KG3), west of Maud Rise (WS2 and WS3) and from the Polar Front (PF3). [The traps were deployed by G. WEFER and his group, University of Bremen]. Table 1 shows the trap location and related technical data.
Barium and aluminum were extracted from sediment trap samples by acid digestion. The samples were analysed by inductively coupled plasma atomic emission spectrometry (ICP-AES).
In order to apply the biogenic barium signal, the total barium was corrected for the non-biogenic portion. For the Atlantic sector of the Southern Ocean, a $(Ba/Al)_{crust}$ ratio of 0.0067 and for the sediments of the Bransfield Strait, which are significantly influenced by volcanic input, a regional $(Ba/Al)_{crust}$ ratio of 0.0021 is used (NÜRNBERG, 1995).

Location	Mooring name	Water depth (m)	Trap depth (m)	Deployment time
Bransfield Strait				
62°15.4´S, 57°31.7´W	KG1a	1952	494	12/01/83-11/25/84
	KG1b		1588	12/01/83-11/25/84
62°20.1´S, 57°28.3´W	KG2	1650	693	12/04/84-11/13/85
62°22.0´S, 57°49.9´W	KG3	1992	687	11/26/85-05/07/86
Maud Rise				
64°55.0´S, 02°30.0´W	WS2	5000	4456	01/20/87-11/20/87
64°54.1´S, 02°33.8´W	WS3	5053	360	11/16/88-02/04/89
Polar Front				
50°07.6´S, 05°50.0´E	PF3a	3785	614	11/10/89-12/23/90
	PF3b		3196	11/10/89-12/23/90

Table 1. Locations and details of trap deployments

RESULTS

In the Bransfield Strait, sediment trap experiments were carried out between November 1983 and May 1986. During the first year, particles were collected in both, an upper and a lower trap (KG1a, KG1b). During the following years, only upper traps were operated (KG2, KG3). The particle flux in the Bransfield Strait is restricted to a short period of 2-8 weeks in austral summer (WEFER *et al.*, 1988), during which the highest Ba_{bio} (max. 447 µg m^{-2} day^{-1}) and aluminium fluxes (max. 109 mg m^{-2} day^{-1}) occurred.

In the Polar Front, particles were collected by two sediment traps at 614 m (PF3a) and 3196 m (PF3b) depth from November 1989 to December 1990. In both traps, the aluminum flux is low ranging from 4 µg m^{-2} day^{-1} in April 1990 to 1259 µg m^{-2} day^{-1} in December 1990. During the austral summer, the Ba_{bio} flux was higher than 100 µg m^{-2} day^{-1} with a maximum (201 µg m^{-2} day^{-1}) during January 1990 in the lower trap.

West of Maud Rise, a time series trap sampled sinking particles at 4456 m depth during 1987 (WS2) and in 360 m depth in 1988/89 (WS3). The seasonal variation of the particle sedimentation in the upper trap attributes to the changing sea ice cover. A lateral transport of particles in the lower trap is revealed by a permanently high particle flux during the entire year (ABELMANN and GERSONDE, 1991, WEFER *et al.*, 1990). The Ba_{bio} flux ranges from 13 µg m^{-2} day^{-1} in June 1988 to 96 µg m^{-2} day^{-1} in February 1988 in the upper trap. In the lower trap, in contrast, the Ba_{bio} flux is permanently around 50 µg m^{-2} day^{-1}. The upper trap shows the lowest aluminum fluxes in the investigated area with a maximum in February 1988 of 33 µg m^{-2} day^{-1}. The aluminum flux is much higher in the lower trap varying around 0.2 mg m^{-2} day^{-1}.

DISCUSSION

Biogenic barium in comparison to other productivity indicators

Corg, opal and carbonate preserved in deep-sea sediments are considered to commonly reflect biological productivity (e.g., SARNTHEIN *et al.*, 1988). The applicability of biogenic barium as a productivity indicator is assessed by comparison with the above mentioned proxies. Figure 1 shows the Corg flux in the upper and lower sediment traps from Bransfield Strait (KG1) and biogenic barium, opal and carbonate fluxes in the upper and lower sediment traps from the Polar Front (PF3). Only those samples were considered, which for the same time period had particulate matter in both the upper and the lower sediment traps. Fluxes were calculated for a period of 303 days (Dec. 31, 1983-Nov. 25, 1984) in the Bransfield Strait, and for 126 days (Nov. 10, 1989-March 16, 1990) in the Polar Front area. Corg, opal, and carbonate data are taken from WEFER and FISCHER (1988), FISCHER (1989), WEFER *et al.* (1990), WEFER and FISCHER (1991), and FISCHER (pers. com. 1994). The highest Babio-flux was observed in the Bransfield Strait, increasing with depth. Similarly, the Babio-flux in the lower Polar Front trap is twice as high than in the upper trap.

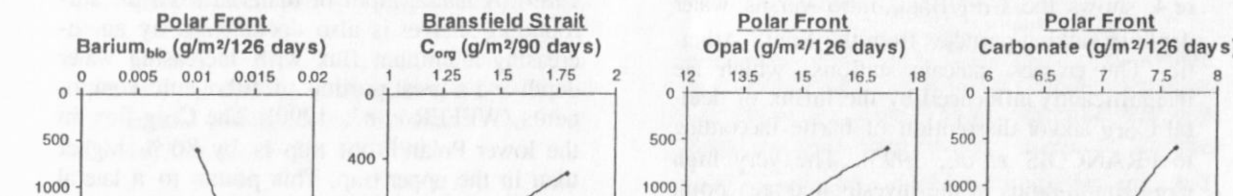
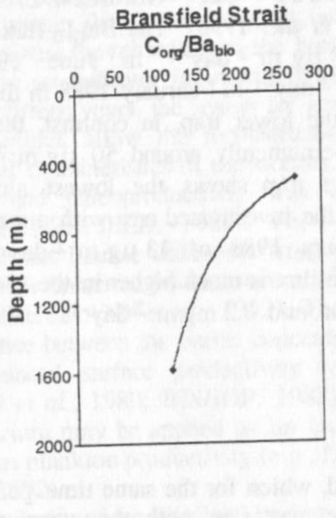


Figure 1. Corg flux in the upper and lower sediment traps from Bransfield Strait (KG1) and biogenic barium, opal and carbonate fluxes in the upper and lower sediment traps from the Polar Front (PF3).

Incresasing concentrations of biogenic barium with increasing water depth point to the high stability of the barite crystals when settling to the seafloor. In addition, the preservation of biogenic barium is better than that of the recycled components Corg, opal and carbonate, indicated by the decreasing fluxes of these proxies with increasing water depth. The Corg/Ba_{bio}-ratio in sinking particles decreases with water depth (Figure 2). This points to the simultaneous uptake of barium during the decay of organic matter and supports the formation of barite in micro-environments as postulated by CHOW and GOLDBERG (1960), DEHAIRS *et al.* (1980), and BISHOP (1988). The strong correlation between biogenic barium and opal fluxes in sediment traps from the southern South Atlantic (Figure 3) further supports the possibility that barite formation takes place in diatom aggregates.



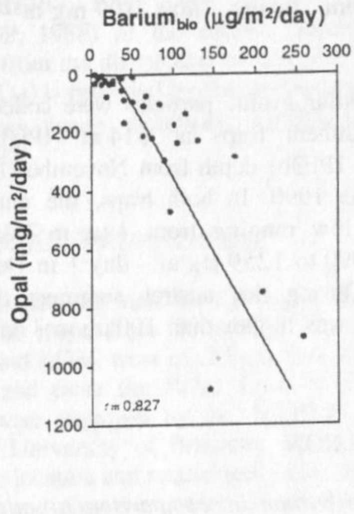


Figure 2. Corg/Ba_{bio}-ratio in sinking particles from Bransfield Strait (KG1) versus water depth. Only those samples were considered, where fluxes of $Ba_{bio}$and Corg are known (at least for a 60 day period, 12/31/1983 - 2/29/1984).

Figure 3. Fluxes of biogenic barium versus opal in sediment traps from the southern South Atlantic. For comparison, only samples from the upper traps (360-693 m water depth) are shown.

The Corg/Ba_{bio}-ratio in settling particles

DYMOND *et al.* (1992) and FRANCOIS *et al.* (1995) showed that the particulate flux of organic carbon covaries with the barium flux. Figure 4 shows the Corg/Ba_{bio}-ratio versus water depth in sinking particles from the South Atlantic. The crosses indicate stations, which are insignificantly influenced by the influx of detrital Corg and/or dissolution of barite (according to FRANCOIS *et al.*, 1995). The very high Corg/Ba_{bio}-ratios in the investigated area point to a lateral input of refractory organic particles into the sediment traps. The Corg-flux in the Bransfield Strait decreases with depth only by 35%, although a decrease of 50% calculated by the equation of SARNTHEIN *et al.* (1988) is expected. Besides, phytoplankton detritus and resuspended marine benthic macroalgae are transported from the Joinville Shelf into the Bransfield Strait (FISCHER 1989). The input of terrigenous Corg can be excluded (FISCHER 1989). A lateral input of material from the surrounding shelves is also documented by an increasing aluminum flux with increasing water depth and a great portion of lithogenic components (WEFER *et al.*, 1990). The Corg-flux in the lower Polar Front trap is by 80 % higher than in the upper trap. This points to a lateral input of particles into the lower sediment trap, which is also confirmed by the increasing aluminum flux with depth. The high geostrophic velocity in the Polar Front of up to 23 cm/s (WHITWORTH III and NOWLIN, 1987) might cause this lateral transport.

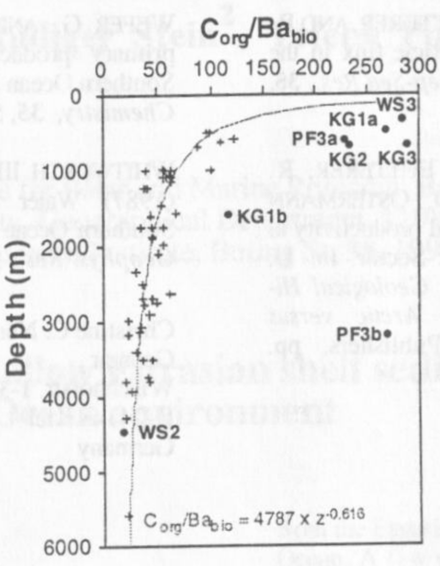


Figure 4. C_{org}/Ba_{bio}-ratio versus water depth in sinking particles from the South Atlantic. Crosses indicate stations, which are insignificantly influenced by the influx of detrital C_{org} and/or dissolution of barite (according to FRANCOIS *et al.*, 1995). This optimal C_{org}/Ba_{bio}-ratio can be described by the power function ($C_{org}/Ba_{bio} = 4787\ z^{-0.616}$): z = water depth (m).

REFERENCES

ABELMANN A. AND R. GERSONDE (1991) Biosiliceous particle flux in the Southern Ocean. *Marine Chemistry,* **35**, 503-536.

BERNSTEIN R. E., R. H. BRYNE, P. R. BETZER AND A. M. GRECO (1992) Morphologies and transformation of celestite in seawater: The role of acantharians in strontium and barium geochemistry. *Geochim. Cosmochim. Acta,* **56**, 3273-3279.

BISHOP J. K. B. (1988) The barite-opal-organic carbon association in oceanic particulate matter. *Nature,* **332**, 341-343.

CHAN L. H., D. DRUMMOND, J. M. EDMOND AND B. GRANT (1977) On the barium data from the Atlantic GEOSECS Expedition. *Deep-Sea Res.,* **24**, 613-649.

CHOW T. J. AND E. D. GOLDBERG (1960) On the marine geochemistry of barium. *Geochim. Cosmochim. Acta,* **20**, 192-198.

DEHAIRS F., R. CHESSELET AND J. JEDWAB (1980) Discrete suspended particles of barite and the barium cycle in the open ocean. *Earth Planet. Sci. Lett.,* **49**, 528-550.

DYMOND J., E. SUESS AND M. LYLE (1992) Barium in Deep Sea Sediment: A Geochemical Indicator of Paleoproductivity. *Paleoceanogr.,* **7**, 163-181.

ELDERFIELD H. (1991) Tracers of ocean paleoproductivity and paleochemistry: An introduction. *Paleoceanogr.,* **5**, 711-717.

FISCHER G. (1989) Stabile Kohlenstoff-Isotope in partikulärer organischer Substanz aus dem Südpolarmeer (Atlantischer Sektor). *Berichte, Fachbereich Geowissenschaften, Universität Bremen,* **5**, 1-161.

FRANCOIS R., S. HONJO, S. J. MANGANINI AND G. E. RAVIZZA (1995) Biogenic barium fluxes to the deep-sea: implications for paleoproductivity reconstruction. *Global Biogeochem. Cycles,* **9**, 289-303.

NÜRNBERG C. C. (1995) Bariumfluß und Sedimentation im südlichen Südatlantik - Hinweise auf Produktivitätsänderungen im Quartär. *GEOMAR Report,* **38**, 1-105.

SARNTHEIN M., K. WINN, J.-C. DUPLESSY AND M. R. FONTUGNE (1988) Global variations of surface ocean productivity in low and mid latitudes: Influence on CO_2 reservoirs of the deep ocean and atmosphere during the last 21,000 years. *Paleoceanogr.,* **3**, 361-399.

VON BREYMANN M. T., K. C. EMEIS AND E. SUESS (1992) Water depth and diagenetic constraints on the use of barium as a palaeoproductivity indicator. In: C. P. SUMMERHAYES, W. L. PRELL AND K. C. EMEIS, editors, *Upwelling Systems: Evolution since the Early Miocene,* **64**, Geol. Soc. Spec. Publ., pp. 273-284.

WEFER G., G. FISCHER, D. FÜTTERER AND R. GERSONDE (1988) Seasonal particle flux in the Bransfield Strait, Antarctica. *Deep-Sea Res.*, **35**, 891-898.

WEFER G., G. FISCHER, D. FÜTTERER, R. GERSONDE, S. HONJO AND D. OSTERMANN (1990) Particle sedimentation and productivity in antarctic waters of the Atlantic Sector. In: U. BLEIL AND J. THIEDE, editors, *Geological History of the Polar Oceans: Arctic versus Antarctic*, Kluwer Academic Publishers, pp. 363-379.

WEFER G. AND G. FISCHER (1991) Annual primary production and export flux in the Southern Ocean from sediment trap data. *Marine Chemistry*, **35**, 597-613.

WHITWORTH III T. AND W. D. NOWLIN JR. (1987) Water masses and currents of the Southern Ocean at the Greenwich Meridian. *J. Geophys. Res.*, **92**, 6462-6476.

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